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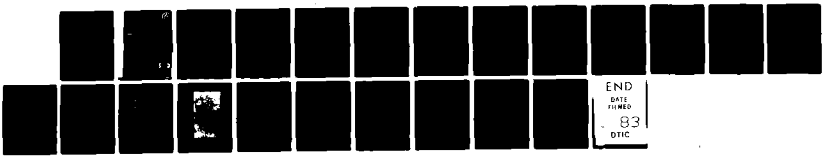

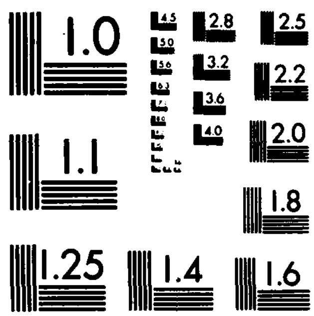

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FABRICATION STUDIES OF TERNARY RARE EARTH SULFIDES
FOR INFRARED APPLICATIONS

[redacted]
RESEARCH DIVISION
LEXINGTON, MA 02173

MAY 1982

FINAL TECHNICAL REPORT
for Period 1 June 1980 to 31 December 1981

Prepared for
OFFICE OF NAVAL RESEARCH
800 N. Quincy Street
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Single Crystal Growth
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A process has been developed for fabricating transparent $CaLa_2S_4$. The key aspect of the process is the synthesis of essentially phase pure $CaLa_2S_4$ powder. This powder is readily sinterable to 95-98 percent density and can subsequently be made transparent by hot isostatic pressing. In-line transmittances of 50, 54, and 56 percent were achieved at 5, 10, and 16 μm for 0.3 mm sample thickness. Absorption coefficients as low as $9 cm^{-1}$ at 12 μm were measured.

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FOREWORD

This report was prepared by Raytheon Company, Research Division, Lexington, Mass., under Contract No. N00014-80-C-0430, entitled, "Fabrication Studies of Ternary Rare Earth Sulfides for Infrared Applications." This work was administered under the direction of the Office of Naval Research, Arlington, VA. Lt. Cmdr. Wayne Savage and Dr. Robert C. Pohanka were the project monitors.

At Raytheon Research Division, this work was performed in the Advanced Materials Department. Mr. Kenneth J. Saunders was in charge of the experimental work. Dr. Richard L. Gentilman was the Program Manager.

The authors would like to take this opportunity to thank Mr. Joe Medici and Mr. Jerry Aucoin for their competent technical assistance and enthusiasm throughout the course of the project. The authors are grateful for the assistance of Ms. M. Ridge in preparing this manuscript as well as the quarterly reports.

During the course of this investigation the authors benefitted greatly from technical discussions with Dr. J. Pappis, Manager of the Advanced Materials Department, and Dr. P. Miles of Raytheon Missile Systems Division, who originally suggested this project.

This Final Technical report covers work performed during the period 1 June 1980 to 31 December 1981. This report was given the Raytheon internal number S-3061.

TABLE OF CONTENTS

1.0 INTRODUCTION AND SUMMARY

Calcium lanthanum sulfide ($CaLa_2S_4$) in particular and other ternary rare earth (TRE) sulfides in general have been shown to have the potential to meet future needs for more durable infrared window and dome materials for the 8-14 micrometer wavelength band.[1] The specific applications of interest are large-size windows for FLIR systems aboard high speed aircraft or hemispherical domes for air-to-surface IR guided missiles such as Maverick. In both types of systems, the strength and hardness of $CaLa_2S_4$ and its intrinsic transmittance in the 10-12 micrometer wavelength regime represent marked potential for improved system performance relative to currently used materials such as germanium or zinc sulfide.

Reported herein are the results of studies conducted over a period of nineteen months at Raytheon Research Division under ONR Contract N00014-80-C-0430. This program has yielded considerable progress toward establishing a fabrication process for $CaLa_2S_4$ windows and domes. Transparent samples with good optical imaging characteristics and no apparent impurity absorption bands between the intrinsic absorption edges have been produced. All fabrication process steps, including powder synthesis, powder consolidation, sintering, hot isostatic pressing, optical polishing, and sample characterization were conducted in-house. A primary consideration was that the processes developed be cost effective and readily scaleable for manufacturing full size hardware.

The initial thrust of the program involved single crystal growth by vapor transport. The objective was to achieve small, high purity, theoretically dense crystals for optical property characterization. However, at approximately that point in time, the basic infrared transparency and usefulness of $CaLa_2S_4$ was confirmed by W. B. White et al.[1] at the Pennsylvania State University. The initial crystal growth experiments were therefore discontinued with the concurrence of ONR because such techniques are not considered practical for fabricating windows or domes.

Thereafter, the majority of the experimental work concerned powder synthesis, sintering, and hot isostatic pressing studies. High purity, essentially phase-pure, and readily sinterable $CaLa_2S_4$ powders were achieved by co-precipitating Ca and La carbonates from a mixed nitrate solution. The resulting carbonates were found to be intimately mixed and readily sulfurized in flowing H_2S at elevated temperature to yield $CaLa_2S_4$ powder.

The $CaLa_2S_4$ powders were consolidated isostatically and then sintered in flowing H_2S. Densities between 81 and 98 percent of theoretical were achieved. The sintered samples were further processed by hot isostatic pressing (HIP) in argon at up to 190 MPa (27,000 psi). Some resulting samples had densities greater than 99.5 percent and were optically transparent with good imaging characteristics.

In-line optical transmittances as high as 50, 54, and 56 percent were achieved at 5, 10, and 16 μm for 0.3 mm sample thickness. Absorption coefficients as low as 9 cm^{-1} at 12 μm were measured.

2.0 EXPERIMENTAL PROCEDURE

2.1 Powder Synthesis and Consolidation

An intimate mixture of Ca and La carbonates was formed by co-precipitation. Initially, the metal ion nitrates were dissolved in water. Then a solution of ammonium.carbonate was added to the nitrate solution to precipitate out Ca and La carbonates. The resulting fluffy, white powder was filtered and dried.

The carbonates were sulfurized in an H_2S atmosphere at 950-1050 C for up to 2 days to form the ternary sulfide. The $CaLa_2S_4$ powder was then isostatically cold-pressed into a 3/4 inch diameter by 3/16 inch thick compact at 170 MPa (25,000 psi).

Sintering studies of the compacts were conducted at temperatures from 1050-1700 C for times up to 16 hours in an H_2S atmosphere.

To eliminate residual porosity, the compacts were hot isostatically pressed at 1000 C for several hours at pressures from 68 to 190MPa (10,000 to 27,000 psi). Figure 1 gives a schematic outline of the overall process of making $CaLa_2S_4$. This could be applied to other ternary sulfide systems.

2.2 Single Cyrstal Growth

$CaLa_2S_4$ in single crystal form would be ideal for measuring intrinsic optical and mechanical properties. As reported previously,[2] the vapor transport approach to growing single crystals had limited success. These results coupled with the continued progress in producing transparent $CaLa_2S_4$ by powder processing led to a de-emphasis of the single crystal growth work.

2.3 X-Ray Diffraction

Fabricated $CaLa_2S_4$ powders were routinely analyzed by X-ray diffraction.*

*Model XRD5, General Electric Co.

PROCESSING OF TERNARY SULFIDES

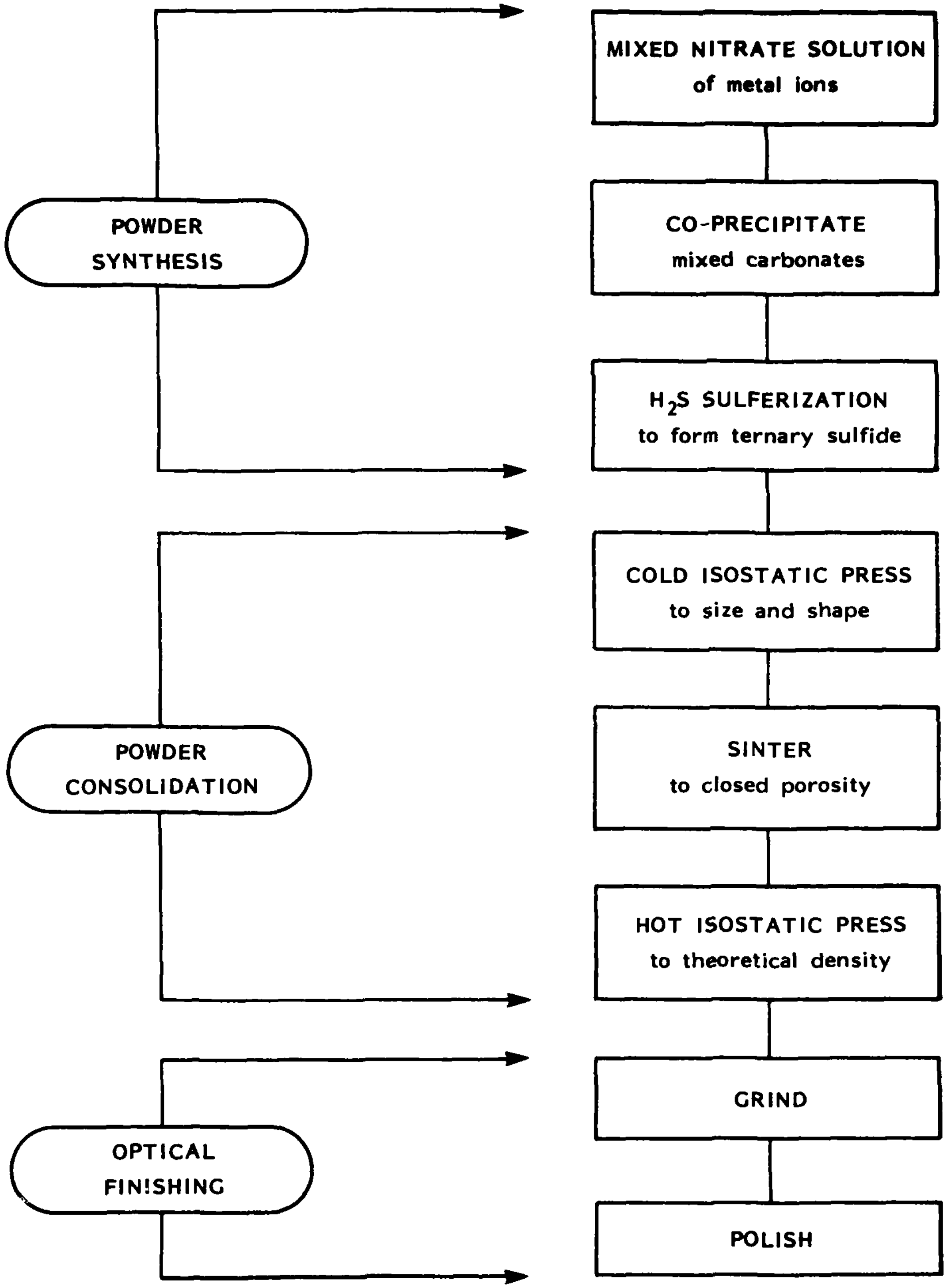

Figure 1. Flow chart of ternary sulfide fabrication.

This was done primarily to determine whether the carbonate powder was completely sulfurized and to check for the presence of binary sulfides.

2.4 Bulk Density

Bulk density was measured on sintered and HIPped samples by the liquid immersion technique using toluene. Percent of theoretical density was then calculated based on a theoretical density of 4.5252 gm/cc.

2.5 Transmittance

Selected samples were sectioned for in-line transmittance measurements using an infrared spectrophotometer.* In some cases two different thicknesses were run in order to calculate the absorption coefficient given by

$$\alpha_w = \frac{-\ln\left(\frac{T_2}{T_1}\right)}{t_2 - t_1}$$

where, α_w = absorption coefficient in cm^{-1} at wavelength w

T_1, T_2 = transmittance of samples 1 and 2

t_1, t_2 = thickness in cm of samples 1 and 2.

*Model 580B, Perkin-Elmer, Norwalk, CT.

3.0 RESULTS AND DISCUSSION

3.1 Bulk Density

Bulk densities ranged from 81 to 98% for sintered samples and 82-100% for HIPped samples. These results helped in optimizing the sintering parameters required to reach the state where all pores of the compact are essentially closed. Theoretical studies by Budworth[3] indicate that the pores in any sintered compact close at a total porosity of about 9%. This suggests that when a sintered compact reaches 91% or more of theoretical density, the residual porosity could be removed by hot isostatic pressing without requiring that samples be encapsulated.

The bulk densities resulting from various sintering and HIPping tre ments are summarized in Table 1.

3.2 X-Ray Diffraction and Microstructure Development

Figure 2a and b illustrate typical X-ray patterns of $CaLa_2S_4$ with and without evidence of CaS presence. The technique itself is limited in that it only identifies phases having concentrations of several percent or more. Evidence of second-phase CaS, not detected by X-ray diffraction is seen, however, by microprobe analysis in some processed samples as shown in Figure 3.

Figure 4a and b show microstructure development before and after HIPping. The as-sintered density of 95% increased to 99.6% after HIPping with virtually no grain growth.

3.3 Transmittance

Figure 5 shows the optimum transmittance results of $CaLa_2S_4$ developed during the contract period of this report. Table 2 lists the absorption coefficient as a function of wavelength for the same material.

Based on the microstructure studies, the presence of second phase CaS appears to be the primary limitation on transmittance of the samples fabricated in this program.

[Following the completion of this program, process development was continued at Raytheon under internal funding. The transmittance of $CaLa_2S_4$ was increased to 62 percent at 11 μm for a 1.2 mm thick samples and 76 percent at 16 μm for a 0.3 mm sample. The absorption coefficient at 10 μm was reduced to 2 cm^{-1}.]

TABLE 1

BULK DENSITIES OF $CaLa_2S_4$ AFTER VARIOUS SINTERING AND HIPPING TREATMENTS

SINTERING				HIPPING			
Sample No.	Temp (°C)	Time (hr)	Theoretical Density (%)	Temp (°C)	Time (hr)	Pressure (kpsi)	Theoretical Density (%)
1-3	1700	2	94.6	990	3	27.5	95.5
				1450	2	27.5	98.6
2-8	1550	16	95.9	1450	2	27.5	98.4
2-10	1450	16	93.9	990	3	26.0	99.3
3-11	1450	16	96.5	990	3	26.0	99.5
3-16	1250	16	96.1	990	3	26.0	99.2
3-20	1150	16	95.0	990	3	26.0	99.4
3-22	1050	16	81.1	990	3	26.0	81.9
3-24	1050	16	92.4	990	3	26.0	99.3

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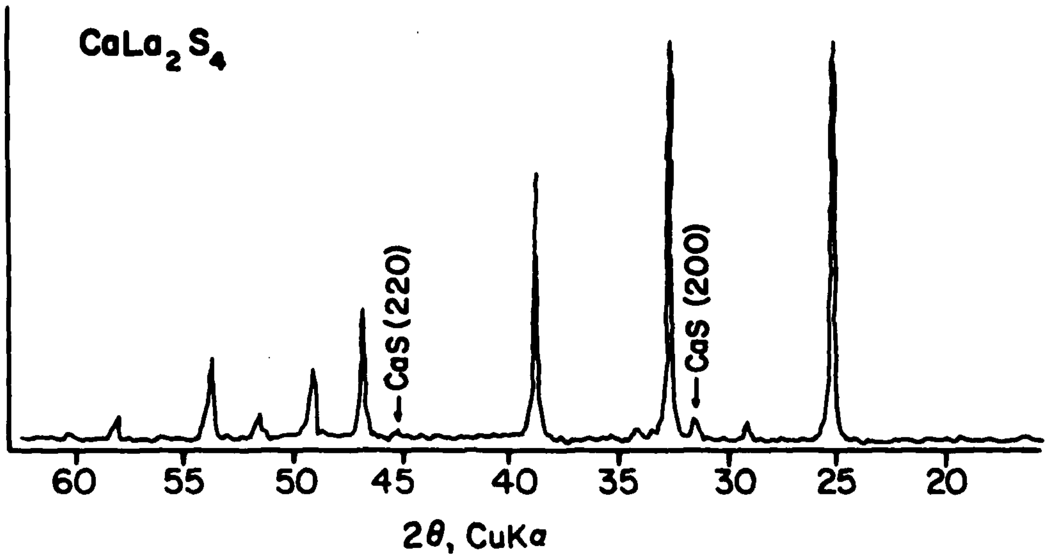
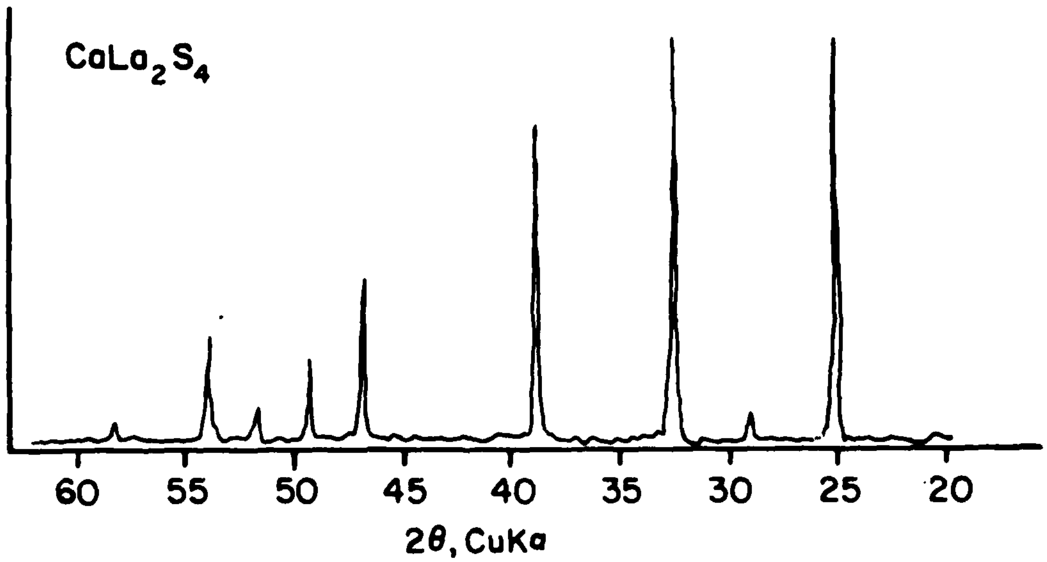


(a)



(b)

Figure 2. X-ray diffraction patterns of $CaLa_2S_4$ showing (a) evidence of CaS and b) no evidence of CaS.

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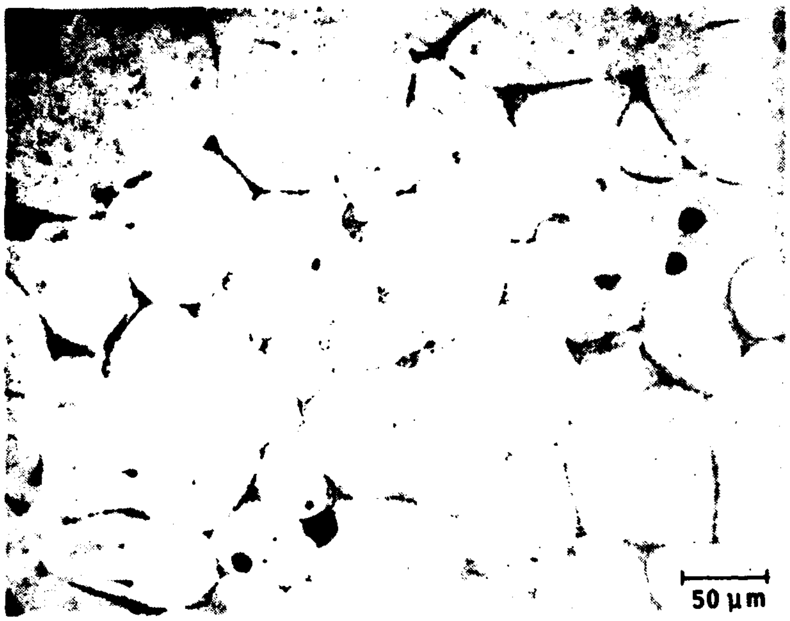
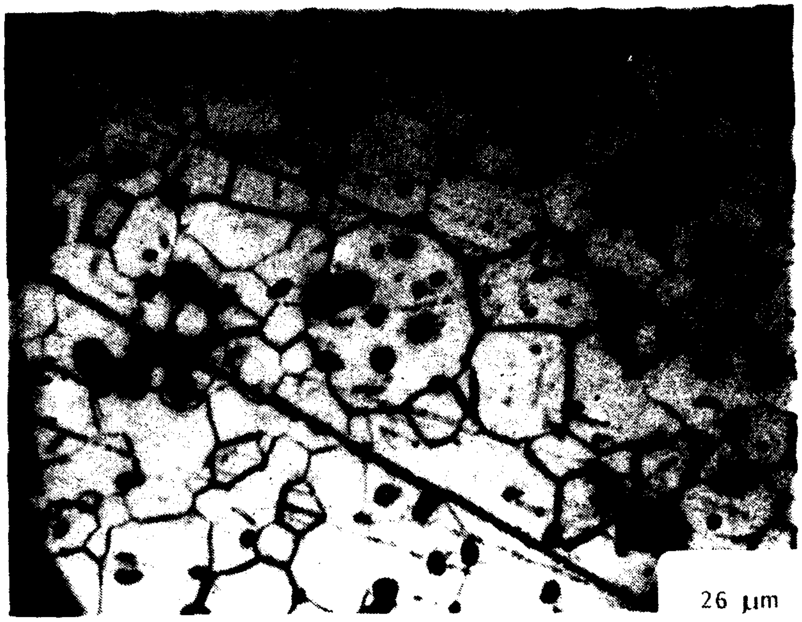


Figure 3. Microstructure of HIPped $CaLa_2S_4$ showing presence of CaS.



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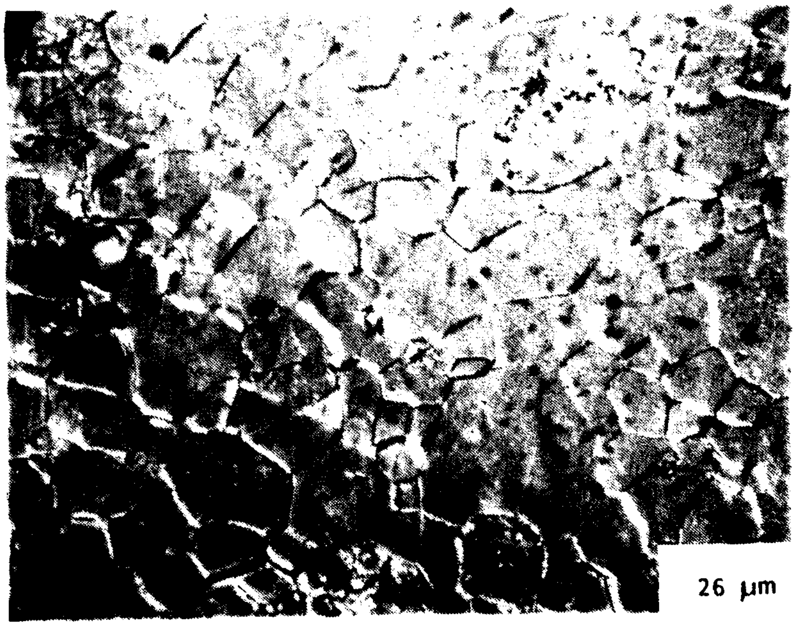

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Figure 4. Microstructure development of $CaLa_2S_4$ before and after HIPping.

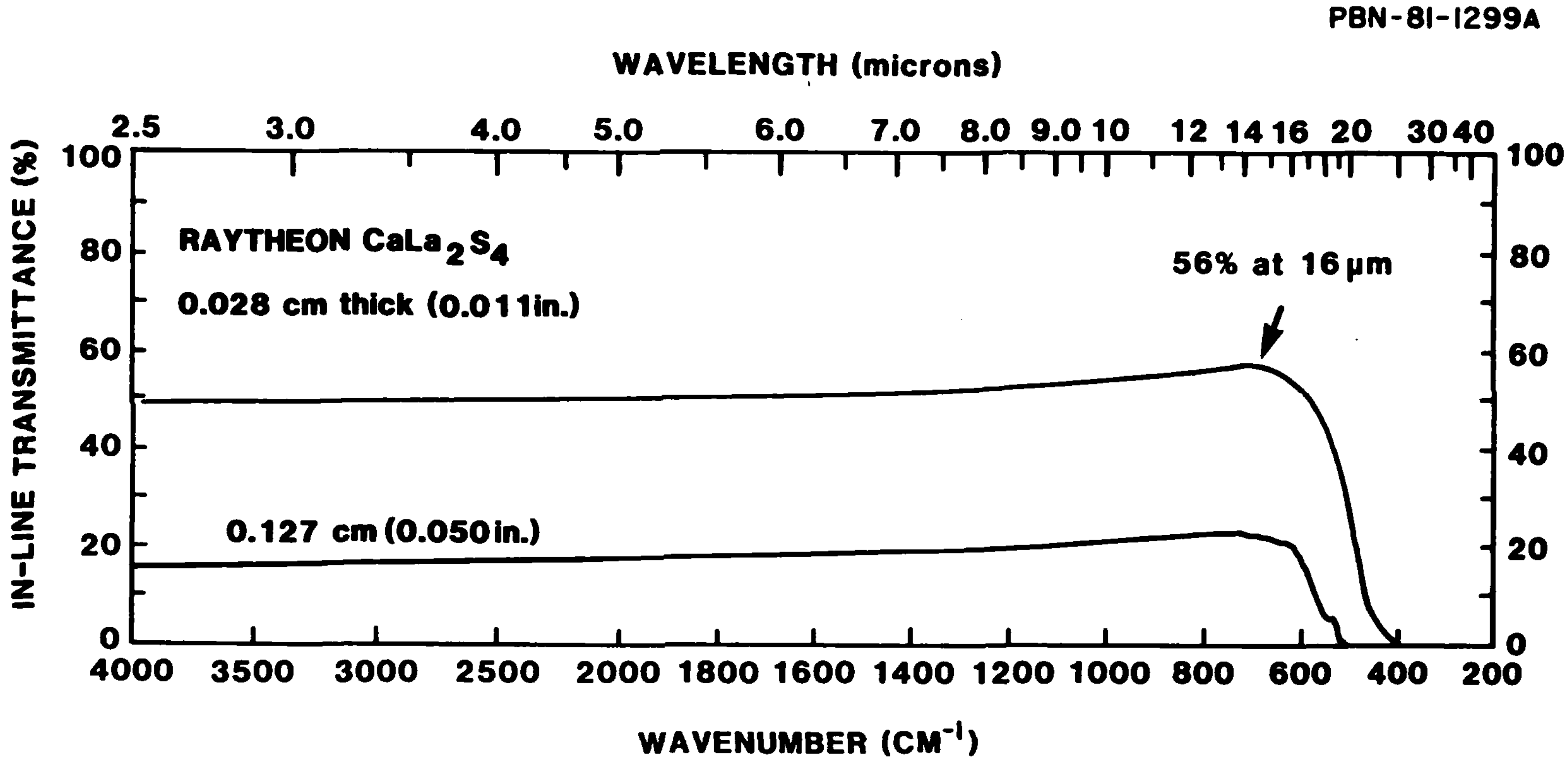

Figure 5. Transmittance results for $CaLa_2S_4$ at thicknesses of 0.028 and 0.127 cm.

TABLE 2

ABSORPTION COEFFICIENT AS A FUNCTION OF WAVELENGTH

FOR $CaLa_2S_4$

Wavelength (μm)	Wavenumber (cm^{-1})	% T_1 0.028 cm thick (0.011 in.)	% T_2 0.127 cm thick (0.050 in.)	Absorption Coefficient (cm^{-1})
4	2500	50	17	11
6	1667	51	18	11
8	1250	52	20	10
10	1000	54	21	10
12	833	56	23	9
14	714	56	23	9
16	625	56	21	10

4.0 CONCLUSIONS

1. Nominally phase-pure $CaLa_2S_4$ was produced by co-precipitation and sulfurization.

2. $CaLa_2S_4$ powder produced was readily sintered to a closed-pore state ($\geq$ 91% density).

3. Sintered samples were subsequently hot isostatically pressed to essentially theoretical density with no evidence of grain growth.

4. HIPped $CaLa_2S_4$ samples were highly transparent with up to 56 percent transmittance at 16 μm for a 0.3 mm thick sample.

5. Further process improvement is required in the fabrication of powders of controlled compositions. In addition, continued optimization of consolidation parameters is required. These parameters include sintering temperature and time and HIPping temperature, time, and pressure.

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2. R. W. Tustison, "Fabrication Studies of Ternary Rare Earth Sulfides for Infrared Applications," Final Report 1 June 1980-31 May 1981, Contract No. N00014-80-C-0430.

3. D. W. Budworth, "Theory of Pore Closure During Sintering," Trans. Brit. Ceram. Soc. 69, 29-31 (1970).

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